Zn-Ni alloy – A probable replacement to Cadmium coating

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1.0 Introduction

Cadmium (Cd) is an important metal which, until recently, found widespread use in a broad range of products and applications, such as electroplating, pigments, polymers, Ni-Cd batteries, TV tubes, solar cells. It offers an excellent corrosion resistance, a sacrificial protection to steel in marine water environment. The high lubricity offered by cadmium permits the cadmium coated fasteners to be installed numerous times and it also reduces the torque during tightening. On account of these properties, it finds important use in aerospace industry for high strength steel fasteners and landing gear components. Despite its beneficial properties, there have been growing concerns on cadmium because of its toxicity and carcinogenicity. Cadmium plating is forbidden under the European RoHS, ELV and WEEE rules and restricted under REACH. Therefore, since past few decades, alternatives for replacing Cadmium are being worked upon. There are several proposed possible alternatives – electrodeposited Zn-Ni alloy and Aluminum, IVD aluminum, electroless nickel-PTFE etc. Zinc-Nickel alloy electrodeposition from acidic and alkaline electrolytes has become the potential leading technology for Cd-replacement both logically and commercially in aerospace industry.

2.0 Why Zinc-Nickel alloy?

The use of Zinc for sacrificial protection of steel is known since ages and is reported largely in literature. However, there are problems associated with voluminous corrosion product in pure Zinc coating hence, and it is not a viable alternate to cadmium coating. In order to achieve good corrosion with pure zinc, coatings need to be thick, around 25 µm which leads to poor weldability and formability. This had led to the search of techniques to improve corrosion resistance of the coating at permissibly lesser thickness still maintaining a similar or higher level of performance.

Iron group metals (Fe, Ni, Co), nobler than zinc helps to increase the electrode potential thereby, the corrosion resistance. Alloys like Zn-Ni, Zn-Fe, Zn-Co, Zn-Ni-Co, and Zn-Ni-Fe have been considered as possible solutions. Of all, Zn-Ni showed superior corrosion resistance compared to pure Zn because of formation of several complex products which act as barrier to the corrosion environment protecting the underlying substrate. Mechanical Properties have been seen to improve with addition of small amounts of Ni (10-20wt %) to Zn deposits. The corrosion resistance of Zn-Ni alloy coating is found to be 3-5 times better than pure zinc coating although the cost is bit higher. The hardness of Zn-Ni alloys is 3-6 times higher than pure Zinc deposits. Ductility of the deposits is also improved.

3.0 Deposition of Zn-Ni alloy coatings

3.1 Electrolyte composition and deposition conditions adopted

Different baths have been opted for electrodeposition of Zn-Ni alloy. Composition of the deposit has a large effect on the functional and mechanical behavior of the coating. Acidic baths are preferred for their excellent corrosion protection, higher (about 95%) current efficiency, and lower plating time. They also provide brilliant luster to the surface due to several additives in the electrolyte. Acidic baths are of two types - sulphate and chloride based. Sulphate type is used for plating simple shapes whereas

chloride type for plating intricate shapes. Chloride type is preferred for their higher throwing power, good anode dissolution and high conductivity. But, limitations of acidic baths are they are not suitable for plating high strength steels and difficult to attain uniform composition and thickness. These drawbacks can be overcome by alkaline baths. Theyare easier to maintain, in addition they also have excellent corrosion resistance and throwing power. But, they have a slower plating rate and lesser current efficiency.

Plating is done by DC and pulse plating techniques. Dense, fine-grained Zn-alloy structures synthesized via pulse electrodeposition leads to excellent corrosion resistance, low coefficient of friction, good coating adhesion, high dimensional consistency, superior surface finish and improved HRE performance.

Some of the commonly employed electrolyte and deposition conditions are mentioned in Table 1.

Table 1. Electrolyte composition and deposition conditions for Zn-Ni alloy plating

Electrolyte	**Composition**		**Plating Conditions**	**Ni% in deposit**
	Element	**Content**		
Alkaline	NaOH	130 g/l	CD = 4 A/dm^2 pH=12 Temp= 30 ^{o}C	3-10% and 16 µm thick
	ZnO	15 g/l		
	$NiSO_4.6H_2O$	5.39 g/l		
	TEA	80 ml/l		
Acidic	$ZnCl_2$	62.5 g/l	CD = 4 A/dm^2 pH=3.5 Temp= 30 ^{o}C	12% and 10 µm thick
	$NiCl_2.6H_2O$	60.7 g/l		
	NH_4Cl	200 g/l		
Acidic	$ZnCl_2$	200 g/l	Peak CD= 3 A/dm^2 T_{on} = 0.25 ms T_{off} =0.75 ms Duty cycle=5% Freq=200 Hz pH=3.4 Temp= 40 ^{o}C	14-20%
	$NiCl_2.6H_2O$	200 g/l		
	H_3BO_3	40 g/l		
	SLS	0.1 ml/l		
Alkaline	ZnO	15 g/l	Peak CD = 2A/dm^2 T_{on} = 1 ms T_{off} =1 ms Duty Cycle =50%	12-13%
	$NiCl_2.6H_2O$	60 g/l		
	NH_4Cl	250 g/l		
	H_3BO_3	20 g/l		

3.2 Mechanism of Codeposition

The presence of an inhibitor in Zn alloy deposition is responsible for the preferential deposition of Zinc. The metal hydroxide formed by hydrolysis due to local pH increase near the cathode in the electrolyte acts as the inhibitor. The activation energy of Zn^{2+} is much lesser than Ni^{2+}. Hence, $Zn(OH)_2$ is formed at a relatively easier rate when compared to $Ni(OH)_2$. This $Zn(OH)_2$ layer acts as a permeable membrane and inhibits the movement of Ni cations to the cathodic surface. This layer is reduced to metallic form for deposition of zinc. This absorbed $Zn(OH)_2$ layer is expected to contain Ni^{2+} cations which are reduced

along with zinc cations to form the alloy layer. Higher content of nickel in the electrolyte leads to higher nickel cations being trapped in the absorbed layer thereby, increasing the Ni content in the deposit. Any parameter which increases pH of the electrolyte should promote Zn deposition based on this mechanism.

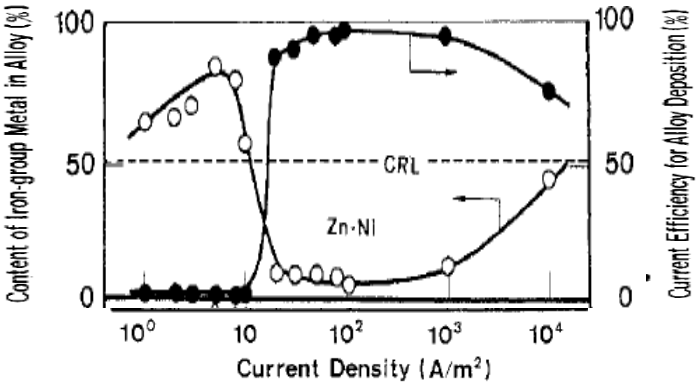

Fig 1.Effect of current density on metal content and cathodic current efficiency

The segmented line in fig 1 indicates the Composition Reference Line (CRL) where the composition in the bath equals that in the deposit. Codeposition condition above CRL is normal because the Ni content in the alloy is greater than in the bath. Whereas below CRL represents the anomalous codeposition. It can also be noticed that at low current densities where normal codeposition occurs, the current efficiency is very less indicating the dominating hydrogen evolution. As the current density is increased, anomalous codeposition takes place with a higher current efficiency.

3.4 Structure and morphology

In vast majority of Zn-Ni industrial applications, the single γ –phase (Zn_5Ni_{21}) is the alloy of interest. Codeposition of 10-20 wt. % Ni is required during plating in order to maintain the presence of the γ-ZnNi phase. Ni content in the deposit depends on the electrodeposition parameters. Changes in morphology, which is a function of deposit composition, are inevitable. The single γ phase structure and dense morphology determine the long term protective and sacrificial properties of the coating.

Various morphologies have been reported for DC plated Zn-Ni alloy coating using acidic electrolyte. Relatively smoother deposits accompanied by finer morphologies were obtained in Ni rich baths. η phase is obtained during the initial stages of plating. With increase in deposition time, it dies out due to preferential growth of γ phase. γ phase is the single predominant phase observed irrespective of the current density applied. However, fine and uniform grain size is obtained at low current densities, while coarse and irregular grains were obtained at high current densities. This trend has been observed in both acidic and alkaline electrolytes during DC plating. An increase in temperature (10-40^{o}C) of deposition increases Ni content in the deposit and it results in more compact and uniform structure. But with further increase in temperature, cracks start to form and the coating degrades.

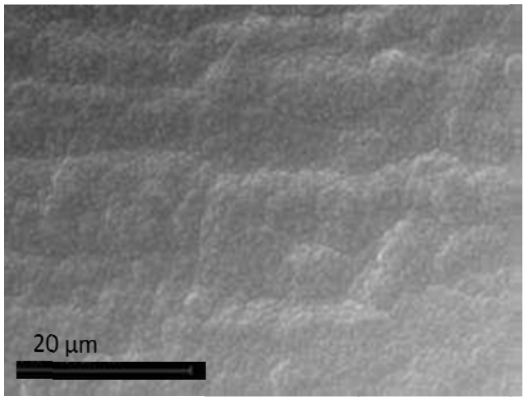

Fig 2 (a)

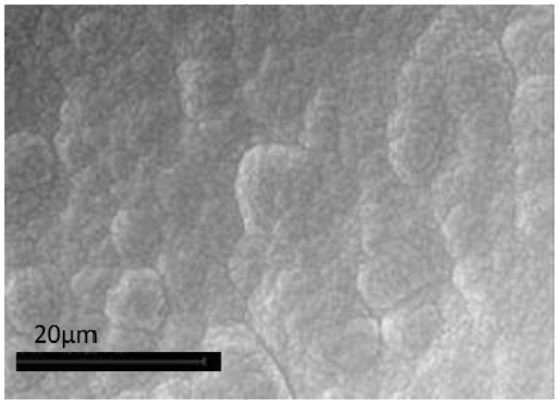

Fig 2 (b)

Fig SEM Micrographs of electrodeposited Zn-Ni alloy produced at (a) T = 30^{o}C, 12wt% Ni (b) T=40 ^{o}C, 13.4wt% Ni

Pulse plated Zn-Ni coating by acidic electrolyte showed that the deposit obtained was uniformly smooth with a nodular fine grained morphology and XRD revealed entire γ phase. The effect of temperature on the structure is similar to that reported for DC deposited coating.

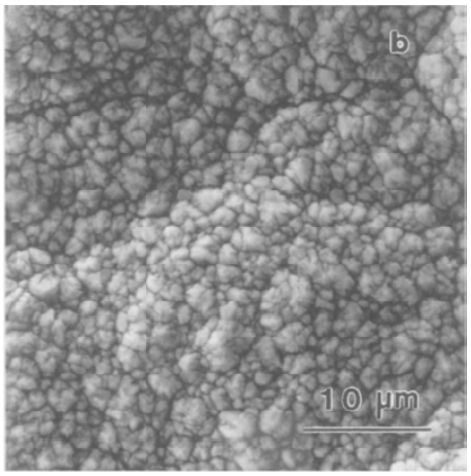

Fig 3 (a)

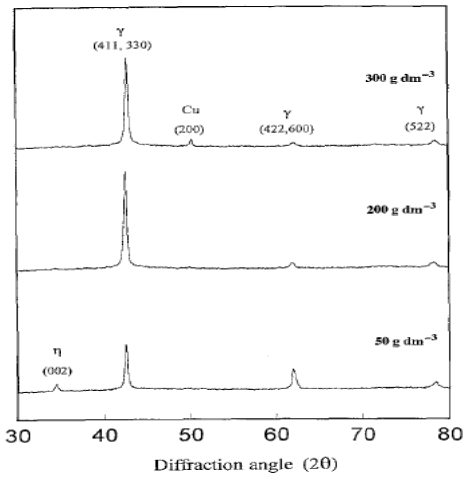

Fig 3(b)

Fig 5.(a)SEM micrograph and (b) XRD of pulse plated Zn-Ni electrodeposited alloy

Hardness

Fig 4 shows the variation of knoop's hardness with Ni content in the DC Zn-Ni obtained from acidic electrolyte. It can be seen that the hardness value increases sharply from 150 KHN at 10Niwt% to 450 KHN at 18 Niwt% i.e., γ Ni_5Zn_{21}. The variation of hardness with duty cycle and frequency in pulse plated Zn-Ni alloy deposits in acidic electrolyte is shown in fig 5. The maximum hardness (414 HV) was obtained at 40% duty cycle and 50 Hz frequency. Generally, pulse plated coatings have higher hardness when compared to direct plated coatings for a given Ni content.

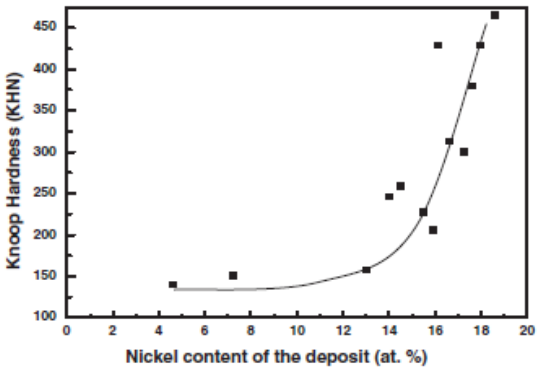

Fig 4. Variation of hardness with Ni content

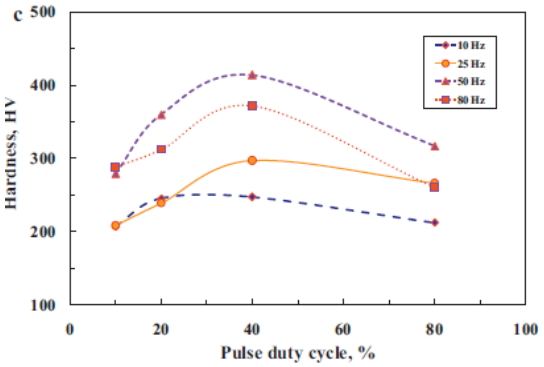

Fig 5.variation of hardness with duty cycle

Corrosion Behavior

Cadmium provides sacrificial protection because of which it has gained importance in aerospace industry. Any replacement to Cd should cater to at least the same corrosion resistance characteristic of Cd.

The presence of single γ phase is responsible for the superior corrosion resistance of these alloys. Ni content required for the formation of single γ phase corresponds to 12-18wt%. A further increase in the Ni content results in brittle and stressed coatings which deteriorates the corrosion behavior.

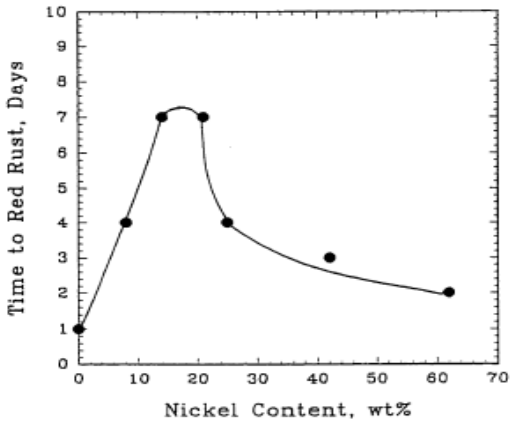

Fig 6. Variation of time to red rust in rust with Ni content

Summary

It can be observed from the above review that Zn-Ni alloy with a Ni content of 12-18wt% exhibits single γ phase. This γ phase is responsible for the improved corrosion resistance, hardness, ductility. Comparison between DC and pulse plated coatings show that the pulse plated coatings exhibit finer and equiaxed grain structure and hence are preferred over DC plated coatings. Coatings obtained from alkaline electrolytes display uniformity in composition and are hence preferred over acidic electrolytes.

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